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Effect of pH on The Adsorption of Pb (II) and Cu (II) Ions from Aqueous Solutions Using a Natural Clay from Ilorin, Kwara State.

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Abstract

The adsorptions of Cu^{2+} and Pb^{2+} ions from aqueous solutions were studied using a natural locally available clay sample obtained from Sango area, Ilorin, Kwara State as adsorbent. The batch technique was employed and the effect of pH on the adsorption processes was studied. The adsorptions of the metal ions were found to be dependent on the pH at which the experiments were carried out. A greater affinity of the clay was observed for Cu^{2+} than Pb^{2+} with maximum adsorption capacities being 944.8 mg/g and 702.6 mg/g respectively. The results indicated that clay in its natural form can be used as an alternative in the treatment waters that are contaminated with these metals.

Keywords: pollution, heavy metals, adsorption, pH, clay.

1. Introduction

Copper is widely used in the industries because it is highly resistant to corrosion and a good conductor of electricity as well as heat. As such, it can be found in many wastewater sources including manufacturing, plating, wire drawing, copper polishing, paint manufacturing, fungicides, algaecides, insecticides and wood preservatives (WHO, 2004) as well as printing operations. It is also present in many kinds of food, drinking water and in air which results into absorption of eminent quantities of copper each day by eating, drinking as well as breathing.

This absorption is necessary because copper is a trace element that serves a crucial role in blood formation (Dara and Mishra, 2011) which is essential for human health. Although humans can handle proportionally small concentrations of copper, excessive concentrations

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however cause eminent health problems (Melichova and Hromada, 2013) like vomiting, diarrhea, loss of strength or, for serious exposure; cirrhosis of the liver (Pure water services, 2013).

Lead is a very soft metal categorized as a “rare element” that has been used in pipes, drains, and soldering materials for many years so much so that, millions of homes built before the 1940s still contain lead (e.g., in painted surfaces) (Dara and Mishra, 2011). As a result of increasing awareness of its toxicity, its large-scale use by various industries has been either curtailed or eliminated but there are still several industrial applications for lead particularly in; construction, alloying, storage batteries, ammunitions, cable coatings, etc so much so that it has been reported that industries produce about 2.5 million tons of lead throughout the world every year (Life extension, 2013; Taylor, 2013). Lead affects almost every organ in the human body particularly the central nervous system in infants and children under age six with effects being the same whether through inhalation or ingestion. Lower levels of exposure, may affect a child's mental and physical growth leading to learning disabilities and seizures while acute lead poisoning in humans causes severe dysfunction in the kidneys, reproductive system, liver, brain and the nervous system (Physicians for Social Responsibility, 2013).

In view of the above, it is only natural that some amounts of these metals are deposited in to the water environment through industrial effluents resulting into pollution which calls for imperative measures in managing industrial wastes effectively in order to control as well as keep the level of the metals within limits that will not be deleterious to the environment. Several chemical and physical methods such as; ion exchange, solvent extraction, reverse osmosis, precipitation and adsorption have been proposed for treatment of wastewater contaminated with heavy metals (Azimi *et al.*, 2017; Barakat, 2011; Ngulube *et al.*, 2017). Among all of these, adsorption onto activated carbon has been found to be more effective than other techniques because of its simplicity in design and capability of adsorbing a broad range of different types of pollutants efficiently. However, commercially available activated carbons are still considered expensive and consequently, adsorption on other adsorbents that are relatively cheaper while exhibiting reasonable adsorption capacity as substitutes has been the focus of many researchers in recent time (Senthil Kumar and Kirthika, 2009).

Clay minerals have been reported to be effective in adsorbing pollutants due to their large specific surface areas and high ion exchange capacities (Melichova and Hromada, 2013; Belarbi and Al-Malack, 2010) such that when compared with other low-cost adsorbents, clays as well as their modified composites have been found to be equivalent or even more efficient in capacity for adsorption of contaminants from water. This is also because of the existence of several types of active sites on the surface, which include bronsted and Lewis acid sites as well as ion exchange sites (Srinivasan, 2011). In addition, their surfaces display interesting properties in their abilities to be charged either negatively or positively depending on the pH of the medium which is the basis for the cation exchange and swelling properties of the minerals (Ismadji *et al.*, 2015). They have been found to be particularly useful for the adsorption of heavy metals such as As, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, and Zn in their ionic forms from aqueous medium with varying adsorption capacities dependent on type of metal and clay used (Srinivasan, 2011).

The entire adsorption process is crucially influenced by the pH of the aqueous solution in which the process occurs (Elmoubarki *et al.*, 2015) as it determines the degree of protonation as well as the specific charge of the exchange sites on the adsorbent thus making the adsorption capacity to be dependent on the pH (Ngulube *et al.*, 2017) and ultimately dictating the proneness of the substrate to adsorption (Tomar *et al.*, 2014). It also governs the different ionic forms that the metal ions can exist in aqueous solutions (Hefne *et al.*, 2008). Hence, the objective of this research was to investigate the efficiency of natural clay (with little pre-treatment as possible) as an alternative for activated carbon in the removal of Pb^{2+} as well as Cu^{2+} from their respective aqueous solutions and to determine the effect of solution pH on the adsorption process. This was especially designed to find alternate simple and low-cost treatment methods for medium and smaller scale industries that lack the expertise as well as the means to afford more sophisticated treatment technologies.

2. Materials and Methods

The Clay sample used for the research was obtained from Sango metropolis of Ilorin, Kwara State, Nigeria. Lead Nitrate ($Pb(NO_3)_2$) and Copper Sulphate ($CuSO_4$) salts were used in the preparation of the aqueous solutions of the respective metals while pH adjustments were done using Nitric acid (HNO_3) and Sodium Hydroxide (NaOH) (Saadi *et al*., 2013). The chemicals were all of analytical grade obtained from Sigma Aldrich and Co.

Sample Preparations

The clay sample was collected and pulverized into powdery form using agate mortar and pestle after which it was washed thoroughly with de-ionized water until a neutral pH was obtained. The powdered clay was then dried in the oven at 105ºC for eight (8) hours and subsequently sieved with a 300 mesh (450micron meter) sieve size. The sample was stored in plastic bottle and no further physical or chemical pre-treatments were carried out prior to the adsorption experiments (low-cost). 100mg/L solutions of both metal ions were prepared by dissolving appropriate amounts of the metal salts in corresponding volumes of de-ionized water.

Batch Adsorption Studies

A 0.5g of the clay sample was weighed accurately into 12 different sample bottles. 5mls of the prepared aqueous $Pb(NO_3)_2$ solution was added to six bottles containing the clay while the remaining six bottles were filled with 10mls of the aqueous $CuSO_4$ solution. The pH of the resulting clay-metal suspensions were adjusted to 2,4,6,8,10 and 12 for bottles 1,2,3,4,5,6 (containing Pb^{2+}) and 7,8,9,10,11,12 (containing Cu^{2+}) respectively after which they were put in the agitator/shaker for easy, equilibrated and mechanical shaking for 4hrs at 35ºC and 165 rpm (rotation per minute). The suspension was later centrifuged for 30mins at 25ºC at 165 rpm and subsequently filtered. The filtrate from each bottle was analyzed by Atomic Absorption Spectrometer for residual metal concentrations. All experiments were carried out in duplicates (Hefne *et al.*, 2008).

3. Results and Discussion

Calculation of Pb^{2+} and Cu^{2+} uptake by Clay Sample

The equilibrium uptake of the respective metal ions in single systems was determined using a mass balance equation (Horsfall, 2003) expressed as:

$$q_e = \frac{V}{M}(C_o - C_e),$$

q_e = metal ion uptake capacity (mg/g adsorbent) at equilibrium, C_e = metal ion concentration in solution (mg/L) at equilibrium, C_o = initial metal ion concentration in solution (mg/L), V = volume of metal ion solution used (L), M = dry weight of adsorbent used (g).

The percentages of the metal ions adsorbed were also calculated using the formula:

$$\% \text{ adsorbed} = \frac{C_o - C_e}{C_o} \times 100.$$

Table 1: The effect of pH on the adsorption of Pb (II) ions.

pH	C_o (mg/L)	C_e(mg/L)	q_e (mg/g)	% Adsorbed
2	100	60.23	397.7	39.77
4	100	37.47	625.3	62.53
6	100	29.73	702.7	70.27
8	100	38.53	614.7	61.47
10	100	66.65	333.5	33.35
12	100	67.30	327.0	32.70

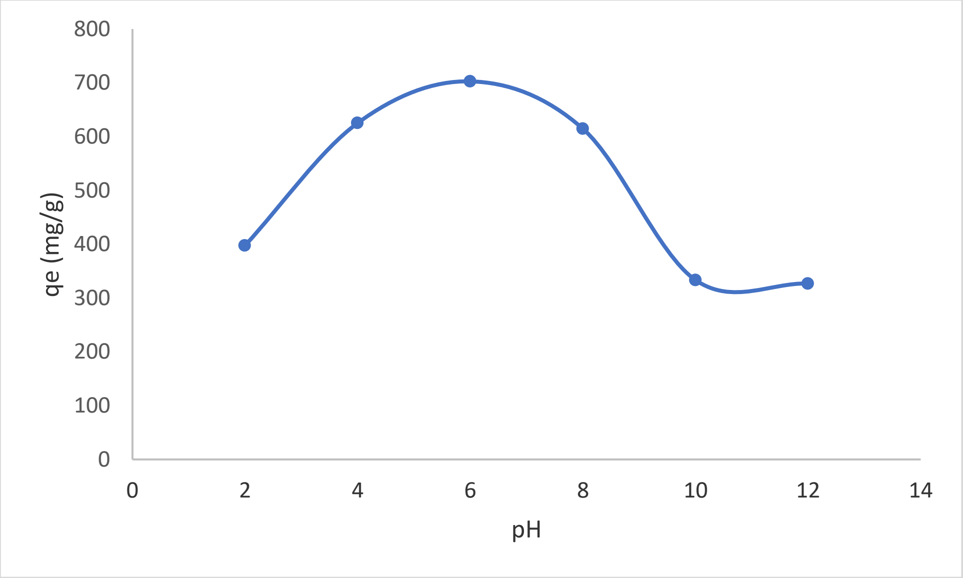

Figure 1: Graph of qe (mg/g) against pH of the adsorption of Pb (II)

Table 2: The effect of pH on the adsorption of Cu (II) ions

pH	C_o (mg/L)	C_e(mg/L)	q_e (mg/g)	% Adsorbed
2	100	23.48	765.2	76.52
4	100	19.82	801.8	80.18
6	100	83.71	162.9	16.29
8	100	33.50	665.0	66.50
10	100	5.52	944.8	94.48
12	100	9.59	904.1	90.41

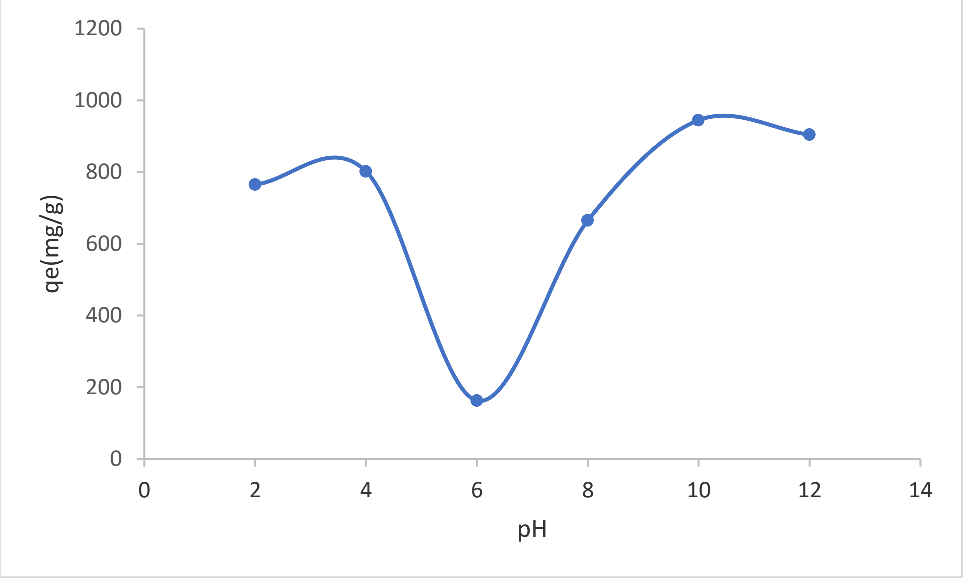

Figure 2: Graph of qe (mg/g) against pH of the adsorption of Cu (II).

It can be observed from the above figures that the clay was able to adsorb both metals reasonably well with more affinity for copper than lead. It can also be deduced that the adsorption of Pb^{2+} increased with an increase in pH of the solution to a maximum around the neutral pH or slightly basic and then decreased with further increase. The adsorption of Cu^{2+} however did not follow a regular pattern as the pH of the solution changes. It can be seen to increase from pH 2 to 4 only to drop drastically around the neutral pH and then increased steadily till pH 12. The maximum adsorption was achieved at pH 10.

Clays are known to exhibit negative surface charges in solutions but this changes as the pH is altered thus the sorption of charged species are affected (attraction between the positively charged metal ion and the negatively charged clay surface) (El-Maghrabi and Mikhail, 2014). It has been postulated (Eba *et al.*, 2013; Dawodu *et al.*, 2012; Rao and Khan, 2017) that at low pH values where there is excess of protons in solution, a competition exists between the positively charged metal ions and the protons for the available adsorption sites on the negatively charged clay surface. However, increasing the pH reduces the concentration of the protons causing more of the positively charged metal ions in solutions to be adsorbed on to the clay surface and thus the percentage removal of the metal ions increases as can be observed to be the case for the two metals studied. On the other hand, excessive increase in pH may lead to a corresponding decrease in the amount of metal ions adsorbed because precipitation of metal hydroxides has been reported to likely occur as the pH of the solution increases (Hefne *et al.*, 2008; Melichova and Hromada, 2013) and this can be the explanation for what occurred in the adsorption of Lead by the natural clay.

A similar trend to the one observed for the adsorption of cu (II) ions in this research was reported by Rao and Khan (2017) only that the adsorption was found to progressively increase at an almost constant rate up to the maximum at pH 10 where as a decline in the rate at close to neutral pH that followed the initial increase was the case here. The maximum adsorption experienced at the alkaline region was surmised to be as a consequence of speciation of Cu^{2+} resulting in to the formation of metal hydroxide which probably made the metal ions to be adsorbed in the form of $[Cu(OH)_2]$ micro precipitates that is the dominant specie beyond pH 6. As a result of this, formation of metal hydroxides might not necessarily impede the adsorption process depending on the metal. This is also supported by another study where the removal of Uranium VI was found to be enhanced by the formation of Uranium hydroxide complexes (Eba *et al*., 2013)

The results obtained in this research are very significant for wastewater treatment purposes. Wastewaters from industries vary greatly in pH (ranging from acidic to basic) depending on the composition and operations of the different sectors of the industry (Wang *et al.*, 2004). As such, wastewater treatment often requires an equalization step where the pH is adjusted prior to treatment but this research has shown that some heavy metals can be removed irrespective of the pH of the solution.

4. Conclusion

It is evident that clay which is a low-cost adsorbent, readily available and easily accessible is relatively efficient in its natural form in the adsorption of the two metals studied. The adsorption process is however affected dramatically by the pH at which adsorption occurred. A careful design and adjustment of the process could be a potential alternative for the treatment of metal polluted waters.

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